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The Fallacy of the Best Two Out of Three

In scientific and engineering investigations a single measurement of an unknown quantity is seldom considered sufficient. Two or more measurements are usually made in order to establish a check on instrumental errors, operator's errors in making readings, and the reliability of the sample. These multiple measurements have two principal advantages: they reveal by their concordance the precision of the measuring process, and they make possible the use of an average of several measurements which will, in general, have a higher precision than one measurement alone. If three measurements are made, it is fairly common practice for students to take the "best two out of three"—averaging the two values closest together and discarding the other. Recently, however, Dr. W. J. Youden of the Statistical Engineering Laboratory at the National Bureau of Standards has shown that this procedure very often leads to less precise results than the averaging of all three measurements together.

Experimental work frequently creates new situations in which the precision of the observations is not known in advance and must be determined from the same data that establish the estimated or average value assigned to the quantity being measured. Although a single measurement cannot yield any estimate of the reproducibility of the value, two measurements do give a primitive indication of their precision. But in an entirely new experimental situation, two measurements may not give a reliable estimate of the precision, since any marked disagreement between the two readings may be due either to the inherent crudeness and inaccuracy of the measurement process or to some accident, such as the gross misreading of an instrument scale, which makes at least one of the measurements greatly in error. With two discordant observations and no other information, it is impossible to decide between these alternative interpretations.

Three measurements are the minimum number that can conceivably reveal one of the measurements to be unreliable in a new experimental situation. Intuition suggests that if two of the three measurements are in close agreement while the third stands apart considerably removed from either of the others, then there may be grounds for suspecting and perhaps rejecting the third value. In terms of the difference between the two in good agreement, how different may the third measurement be before it should be suspected? Since this problem is important to all who make and interpret measurements, it is a little surprising that an answer has only recently been found.

An approximate solution has been obtained in the Bureau's statistical engineering laboratory through an empirical study of triads drawn at random from a large group of measurements constructed to conform to the characteristics of a normally distributed set entirely free from any gross errors. In this way, it is possible to examine a great many sets of three measurements and to determine, for example, how often the two differences between adjacent values in a set of three measurements will bear a ratio of 5 to 1, 10 to 1, 20 to 1, or any other ratio that might be considered unlikely in the normal course of events. If only 1 out of 100 sets of

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three measurements contained a measurement differing from the others by as much as five times the difference between the two closest, then such an observation might reasonably be discarded in actual experimental data. But the empirical study actually showed that a rather unbalanced spacing between three measurements occurs quite frequently. In fact, the ratio of the two differences was as much as 16 to 1 in 10 percent of the sets of three measurements. In this connection, it is important to note that high ratios can result when two of the readings are very close or coincident while the third is not far removed.

The mathematical solution of this problem has been obtained by J. Lieblein and the frequency of occurrence for various ratios of the two differences has been calculated. The following table shows, for certain ratios, the results of an empirical sampling study of 400 sets of three measurements compared with those predicted by the exact mathematical solution of the problem.

Ratio of large to small difference	Frequency in 400 sets	Theoretical frequency
4.0 or more	149	145. 2
9.0 or more	76	69. 4
19.0 or more	38	33. 9

These results reveal that in an average of one out of every twelve sets, one of the measurements will be at least 19 times farther away from its neighbor than the difference separating the two closest. Since in every 12 sets 1 shows such a spacing for measurements with no gross observational errors, it appears that measurements that should be retained are often dropped from the record. The problem of deciding on standards for the rejection of observations is one of long standing. Statisticians are again attacking this problem and, in the light of recent advances in the theory of small samples, considerable progress can be expected.

TECHNICAL NEWS BULLETIN

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CHARLES SAWYER, *Secretary*
NATIONAL BUREAU OF STANDARDS
E. U. Condon, *Director*

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Contents

Electronic Instrument Tests Geiger Counters

An electronic gating instrument has been designed and constructed by Louis Costrell at the National Bureau of Standards for the accurate determination of the deadtime and recovery characteristics of Geiger-Müller counters.[1] A knowledge of the operating characteristics of Geiger counters is essential whenever they are to be used for precise measurements of nuclear radiation. The deadtime and recovery characteristics are important, not only because the errors in counting depend on them, but also because they are intimately associated with the electrical discharge process.

When incoming radiation causes an ionizing event in a Geiger counter, negative electrons are attracted to the positive wire. Since the electric field near the wire is extremely high, electrons released in the initial ionization gain enough energy to release additional electrons from neutral atoms that lie in their paths, and these electrons in turn dislodge more electrons as they travel toward the wire. This electron stream produces a negative voltage pulse across the terminals of the counter.

The highly mobile electrons reach the positive wire of a Geiger counter within a fraction of a microsecond after ionization has occurred. At the same time, the heavy positive ions begin moving toward the negative outer cylinder. These positive ions still remain in the vicinity of the wire long after the electrons have reached it. They form a sheath around the wire and reduce the field intensity below the value required for another avalanche to take place. If a particle enters the counter while the ions are still close to the collecting wire, Geiger action cannot occur. As the sheath of positive ions moves slowly outward, the electric field around the wire increases, reaching its normal value when the ions arrive at the outer cylinder.

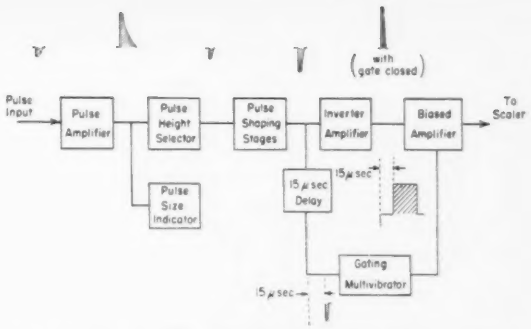
The deadtime is defined as the time interval after a

[1] For further technical details see, Accurate determination of the deadtime and recovery characteristics of Geiger-Müller counters, by Louis Costrell, J. Research NBS **42**, 241 (1949) RP1965. Available from the Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C. 10 cents.

pulse has occurred, during which the counter is insensitive to further ionizing events. Physically it is the time required for the positive ions to travel far enough from the wire to let Geiger action resume. Similarly, the recovery time is defined as the time interval that must elapse after a pulse has occurred before a full-size pulse can again occur; physically it is the time required for the positive ions to reach the counter wall. Both the deadtime and the recovery characteristic of a Geiger counter, as well as the input sensitivity of the associated circuits are involved in the "resolving time," defined as the minimum time interval by which two pulses must be separated to be detected as separate pulses by the counter and its accessories.

Since nuclear disintegrations occur in a random manner, there is a finite probability of two disintegrations occurring within any given time interval. Since the counter is dead for a short period after each pulse, some disintegrations are not detected, resulting in a discrepancy between the number of particles entering the counter and the number of counts recorded. For example, if the counting rate is 100 counts per second, using a counter with a resolving time of 300 microseconds, 3 percent of the ionizing radiation will not be recorded. For the same counting rate, a counter with a resolving time of 1,000 microseconds will give an error of approximately 10 percent. Resolving time errors are automatically compensated for if the counter is calibrated against a radiation standard of the same intensity as the sample under test. However, if the standard and test sample differ appreciably in intensity, such compensation does not occur.

With the Bureau's electronic gating instrument it is possible to study the pulses that occur in the time interval between the end of the deadtime of a Geiger counter and the end of a predetermined gating period. In practice, the counter under test is exposed to a steady source of radiation, and the number of accepted counts is recorded for various gating times. As the gating time is reduced the number of counts decreases. The deadtime is obtained by plotting a curve of accepted counts versus gating time and extrapolating to find the intersection of the curve and the time axis. By adjusting the gating instrument to accept only pulses above a certain size, it is possible to obtain similar curves for which the time-axis intercepts represent the recovery time of the counter for various pulse amplitudes.



An electronic gating instrument determines accurately the deadtime and recovery characteristics of Geiger-Müller counters. Knowledge of these characteristics is essential whenever the counters are used for precise measurements of nuclear radiation.

When the gating instrument is in operation, random pulses from a Geiger counter are fed through the pulse amplifier to the pulse height selector and pulse shaping circuits to give sharp negative pulses of uniform height. These negative pulses follow two paths: One through an amplifier to a heavily biased stage and the other through a delay circuit to a gating multivibrator. An initiating pulse entering the system finds Channel 1 blocked by the heavy bias. But by way of Channel 2 it trips the multivibrator and opens Channel 1 for pulses to pass. Because of the delay in Channel 2, Channel 1 is not opened until the initiating pulse has died away. The delay used is 15 microseconds. Subsequent pulses find Channel 1 open, go through it, and are counted. After a time determined by the circuit constants of the multivibrator, Channel 1 is blocked off again and the whole process is repeated. For the usual counting rates, the probability of having more than one pulse during the interval while Channel 1 is open is very small. In effect, the system selects pairs of pulses with a time separation less than a selected value determined by the setting of the controls on the multivibrator, and one count is recorded for each such pair received. In the determination of recovery curves the bias voltage of the pulse height selector is adjusted to discriminate against pulses of less than a selected size.

Laboratory Wear Test for Automotive Gear Lubricants

Recent investigations by S. A. McKee, J. F. Swindells, H. S. White, and Wayne Mountjoy of the Bureau's engines and lubrication laboratory have shown that the SAE extreme-pressure lubricants testing machine can be adapted to measure accurately the wear obtained with various automotive gear lubricants under simulated service conditions.[2] This apparatus—originally designed for testing load-carrying capacity of gear lubricants under fixed high-speed and shock-loading—provides a sensitive means for the evaluation of lubricants with respect to wear at high torque and low-speed operation. The new test therefore makes it possible to detect any significant difference in the performance of lubricants meeting the requirements of the same specifications.

Of the various laboratory testing machines commonly

[2] For further technical details see "Laboratory wear tests with automotive gear lubricants," by Samuel A. McKee, James F. Swindells, Hobart S. White, and Wayne Mountjoy, J. Research NBS42, 125 (1949) RP1955.

used in the study of automotive gear lubricants, the SAE machine more nearly simulates gear operation.[3] Two contacting cylindrical test cups of this machine are rotated at different speeds under load, providing a combined rubbing and rolling action that is typical of loaded gear teeth. A further similarity is a constantly changing line contact with respect to the surfaces of both cups; hence no one point on the periphery is under continuous stress.

The machine is particularly adaptable for wear tests, because the test specimens are of such size and shape that accurate indications of wear may be obtained by determination of loss in weight. Also, any wear that occurs on the test cups does not materially affect the area of contact under a given load. On the other hand, the method of lubricating the test surfaces is not especially suitable for long-time tests, and it was necessary to modify the machine in this respect.

Although the primary objective in modifying the lubrication system was long-time operation, it was decided also to provide better temperature control of the upper test cup. In the original machine, the lower test cup is supported half immersed in a small oil box. Lubrication between the two cups is effected by the oil carried up as the lower cup rotates. Since only the lower cup is cooled by immersion in the oil bath, the upper cup runs at a considerably higher temperature. This is usually quite noticeable in the load-carrying capacity tests. For this reason, an additional oil reservoir of larger capacity and a circulating system were provided for applying a stream of oil to the upper test cup.

In the modified lubrication system the oil being tested is drawn from a reservoir by a motor-driven pump and delivered through a ¼-inch pipe to the top of the upper test cup, which is covered by a special oil splash guard. The oil then drains to the oil box, which is fitted with two ¼-inch overflow pipes so located that the oil level in the box partially immerses the lower test cup. The oil from the overflow falls into open fittings in the ¾-inch drain pipe and returns to the reservoir. Heat is applied to the oil reservoir and delivery pipe, whereas thermocouples in the oil box and oil reservoir provide a means for temperature measurement and control. Counterbalanced overflow pipes, splash guards, and an oil thrower prevent excessive oil leakage around the test cups and oil box.

The lubricants used in the Bureau's investigations were SAE 90 grade and included a Navy contract 1080 mineral oil, five lubricants conforming to U. S. Army Specification 2–105B, five lubricants conforming to Federal Specification VV–L–761,[4] and one lead-soap active-sulfur lubricant.

In these wear tests, the upper cup is driven at a speed of 500 rpm with a 3.4 to 1 gear ratio between the upper and lower cups, thus providing a 2.4 to 1 ratio of rubbing to rolling at the contacting surfaces. The specimens, steel Timken test cups (T–48651), have an average (root-mean-square) surface roughness of from 25 to 30 microinches as measured with the Profilometer. Each lubricant sample (2 quarts) is circulated at a rate of about 500 grams per minute. With a constant oil temperature of 225° F, tests were made at constant loads of 90, 135, 180, and 225 pounds (scale readings). The loading system is such that the corresponding loads on the 2-inch diameter by ½-inch test cups are ten times the scale readings. Tests were also made at 250° F and 180-pound load. The above conditions approximate the range of conditions covered in the usual high-torque low-speed gear tests.

The SAE extreme-pressure lubricants testing machine was modified for the Bureau's wear tests with automotive gear lubricants by adding an oil reservoir (*A*) and a circulating system for applying oil to the upper test cup (covered by guard *D*). Temperature is effected though heaters *J* and *K*, and thermocouple *H*.

The test cups are weighed before and after each period of operation, the loss in weight being used as a measure of wear during the test period. At the beginning of the Bureau's investigations, weighings were made at frequent intervals, and the tests were run for as long as 75 hours. It was found, however, that representative data could be obtained by operating for about 25 hours, with weighings after 4, 11, 18, and 25 hours of operation.

In general, the data obtained in these tests indicate that there is a run-in period of high rate of wear for a few hours, after which the wear settles down to a fairly constant rate. In a graphic plot of such data the straight portion of the curve usually is well established by 25 hours of operation. The slope of this portion of the curve is more significant from the standpoint of estimating gear life than the observed loss in weight for any given length of time. At the higher loads the rate of wear with some of the lubricants showed a marked increase, whereas with others there was little effect.

[3] S. A. McKee, F. G. Bitner, and T. R. McKee, SAE Trans. **33**, 402 (1933). See also William S James, SAE Trans. **47**, 312 (1940).

[4] U. S. Army Specification No. 2-105B, Lubricant, gear, universal (Mar. 28, 1946); Federal Specification VV-L-761 for Lubricants; enclosed-gear, hypoid-gear, and other types (Nov. 28, 1947).

Although wear data with hypoid gears are not available for a direct comparison, it is believed that these results are in reasonable agreement with the known service performance with these lubricants. The wear with the mineral oil was low up to the point where it would not carry the load, whereas with the lead-soap active-sulfur lubricant (which will carry a high shock load) the wear was relatively high at all but the lightest load.

In most of the tests, Profilometer readings of the surface roughness of the test cups were obtained at intervals during the test run. For those tests where the rate of wear was relatively low, the roughness decreased in the run-in period and tended to level off in a range between 10 and 20 microinches. As the rate of wear increased, there was a trend for the roughness to increase. This was especially noticeable in cases of excessive wear where there was definite "ridging" of the cups, which in some cases was beyond the range of the Profilometer.

In connection with a brief study of the effect of the original surface roughness of the cups on the rate of wear, test data were obtained with the mineral oil and one of the Army specification lubricants operating at 225° F and 135-pound load, using cups with original roughnesses of 14, 28, and 35 microinches (rms). Such operation brought the roughness of the cups fairly close together. It was also noted that while the run-in wear tended to increase with increase in roughness, the final rate of wear was practically independent of the original surface roughness over the range covered. Comparable data may therefore be obtained, even when reasonable differences in the surface roughness of the cups exist.

Besides offering a sensitive measure of the rate of wear with different commercial gear lubricants, the new test provides evidence of run-in wear that is of considerable importance. This should be taken into account in the evaluation of lubricants with respect to wear. Still another advantage is that the rate of wear after the run-in period is not materially affected by the original roughness of the test cups, as is the case with the usual load-carrying capacity tests with this machine.

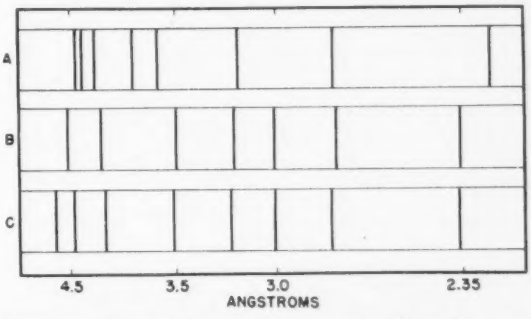
The lubricants containing the more chemically active additives for withstanding higher shock load tend to show the greater wear. This is in agreement with the known service performance of some of these lubricants, particularly the active-sulfur lubricant and the nonadditive mineral oil.

The Structural and Physico-Chemical Properties of Soaps and Detergent Materials

Electron microscope and X-ray diffraction studies of soap crystals, carried out at the National Bureau of Standards, have revealed characteristic features for each type of soap molecule that can be used for its identification and analysis. The electron microscope also indicates the individual soap forms that are present in a mixture, such as a commercial soap prepared from mixed fats or oils; this is not always possible with the X-ray spectrometer because of the nature of the diffraction patterns obtained. When considered in conjunction with physico-chemical measurements of aqueous soap solutions, these data offer an explanation of the mechanical process of cleansing, and at the same time suggest a basis for evaluating the cleansing power of the different types of soap.

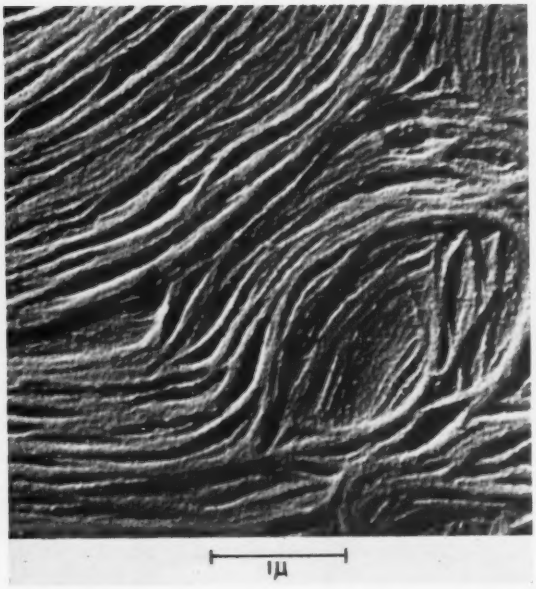
Although soaps and other kinds of cleaning materials have been in common use for centuries, there are no universally accepted quantitative methods for determining their washing or cleansing power. Considerable data are available in the literature on the structural and phase [5] behavior of pure alkali soaps in the solid state, as well as on the physico-chemical characteristics of their aqueous solutions. Soaps and the newer synthetic soapless detergents, however, are in many cases bought only on the basis of appearance and texture: the quantity of suds they produce; and, with some critical purchasers, their action on the skin and hands. The present investigation was conducted by Gopal S. Hattiangdi, in cooperation with members of the Surface Chemistry and the Constitution and Microstructure Laboratories at the National Bureau of Standards, to apply some of the newer scientific techniques to the problem.

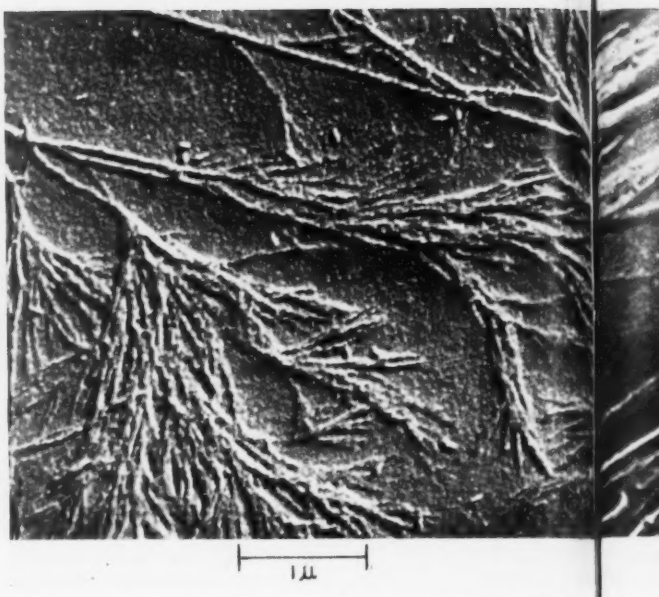
Commercial soaps contain, for the most part, the sodium or potassium salts of the higher fatty acids.



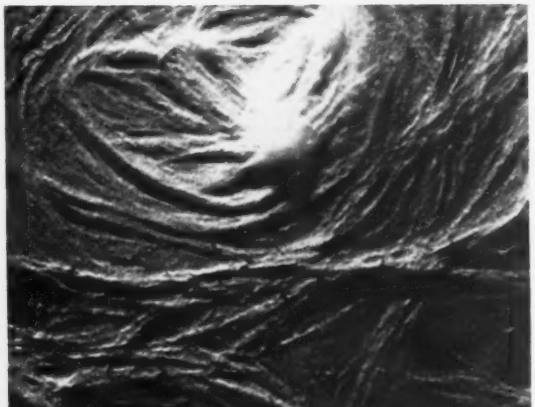
Important X-ray diffraction short-spacing lines for pure sodium palmitate *(A)*, sodium oleate *(B)*, ad a typical commercial toilet soap *(C)*. The single long-spacing for the toilet soap, not indicated in this figure, is intermediate between the values for the two pure soaps but is more closely related to the palmitate. The short spacings for the commercial soap are comprised essentially of the strong lines for the individual pure soaps and the pattern resembles one to be expected from superposition of those for the pure palmitate and oleate.

[5] A phase is defined as any portion of a system which is homogeneous throughout, which is bounded by a surface, and which may be mechanically separated from the other portions or phases.





Electron micrographs of soaps and soap mixtures reveal featu hat ser selves (*top row*) and for the identification of the components ommer *right). Top row, left to right:* Sodium oleate (total magnifi n X20,((total X19,200, el. X5200, opt. X3.7); sodium laurate (X19,8 X11,000, el. X5200, opt. X2.1). The typical structure of m olea X22,000, el. X10,500, opt. X2.1) and of sodium palmitate in oilet soa

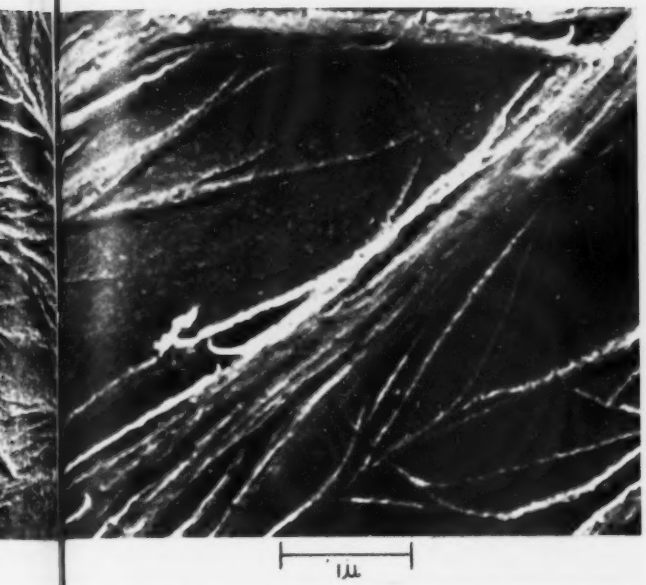


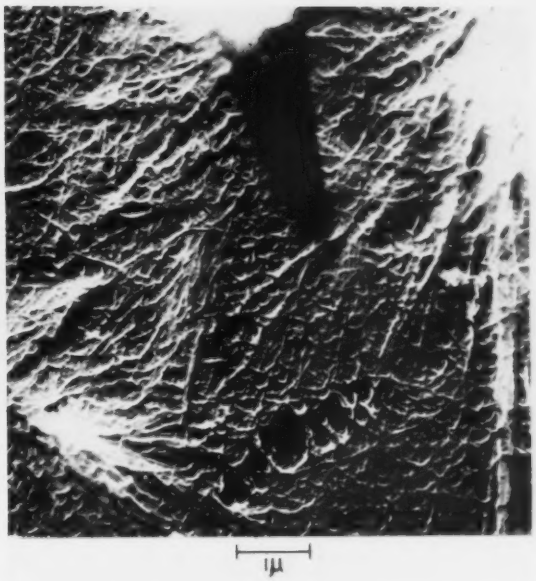
Small amounts of inorganic salts, organic compounds, and other additives may also be present to enhance some special property of the product. The synthetic detergents, on the other hand, are mostly soapless compounds obtained by the sulfonation, sulfation, or similar treatment of various types of organic molecules. A total of 30 typical commercial soaps (toilet, medicated, glycerin, coco, washing or laundry, and shaving varieties) and 6 popular synthetic soapless detergents were included in the investigation. In addition, for the electron microscope and X-ray diffraction studies, a number of pure soaps were prepared directly from their fatty acids.

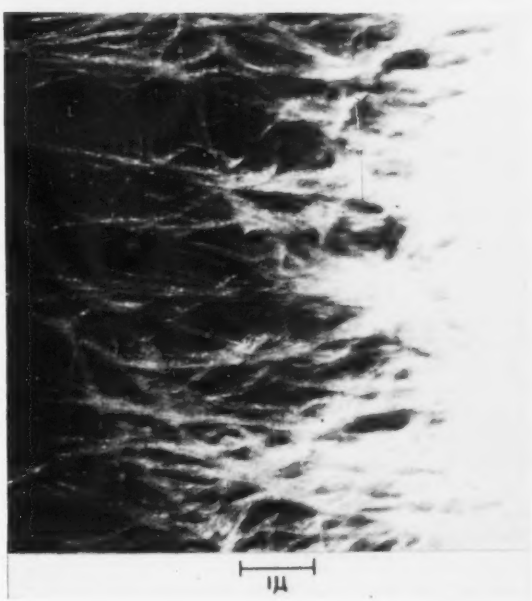
The differences in structural arrangements between soaps and between soap phases may be determined by examining surface details. Several previous investigators have used the polarizing microscope at about 200 to 400 magnifications as a valuable adjunct to visual observations. The electron microscope, with its high resolving power (approx. 100 A), has been used with considerable success in recent years to examine the surface details and structure of a variety of systems and, in conjunction with the metallic-shadowing technique, yields additional significant information. The approach to the present study by Hattiangdi and Max Swerdlow was to obtain first the morphological differences between several pure alkali soaps and then to examine the possibility of characterizing commercial soaps on the basis of these observations.[6]

The most characteristic feature of the electron micrographs for the pure soaps is an interlocked mesh of fiber bundles of varying diameters and different degrees of twist but with a general tendency toward retaining both a criss-cross and a parallel structure. The diameters of the soap fibers depend upon the nature of the soap, concentration, rate of crystallization, and other factors. Consequently no measurements and interpretations in terms of absolute units were made. An attempt has been made, however, to represent schematically the growth of fibers and fiber bundles in terms of molecular packing. Packing of the soap molecules end to end,

[6] Characterization of alkali soaps by electron microscopy, Gopal S. Hattiangdi and Max Swerdlow, J. Research **42**, 343 (1949) RP1975.







l featu hat serve for characterization of the pure alkali soaps them- ponents ommercial soaps of unknown composition (*lower left and* nagnifie X20,000, electronic X9500, optical X2.1); sodium stearate rate (X19,800, el. X5200, opt. X3.8); sodium palmitate (total re of m oleate is evident in the toilet soap (*lower left*) (total tate in ilet soap (*lower right)* (total X11,000, el. X5200, opt. X2.1).

probably a minimum of ten, determines the "width" of the fibers. The association of the soap molecules in a direction perpendicular to the long axis of the soap molecules but in the plane of the hydrocarbon chains takes place almost indefinitely and results in the "length" of the soap fiber. The "height", or "thickness", of the fiber depends upon the number of soap molecules packed in a direction perpendicular to the plane of the carbon atoms but parallel to the long axis of the soap molecules.

Another outstanding characteristic revealed by the electron microscope is that each pure soap exhibits unique and distinct features, such as a curdy mass, an octopean mass, or filamentous, hairy, frond-like, or sheaf-like formations. These are probably the result of a type of structural unit, such as a micellar grouping within the soap fibers, and are related to the mosaic structure of the crystal surfaces or to the crystal structure of the individual soap phases. Whatever the interpretation, these patterns serve as excellent guides for a quick characterization of the pure alkali soaps and for the identification of the components of commercial soaps of unknown composition. Thus, electron micrographs for the toilet soaps reveal distinct forms for both sodium palmitate and sodium oleate. The shaving soaps are characterized by forms typical of sodium palmitate. The laundry (washing) soaps exhibit forms that cannot be definitely identified with those for any of the pure soaps investigated.

X-ray diffraction patterns were also obtained [7] with a Geiger-Müller X-ray spectrometer in order to determine the molecular arrangements or phases present in commercial soaps. When a beam of X-rays is directed at a glancing angle against a soap surface most of it is reflected at the same angle, but a few rays are diffracted at other angles. The intensity of the diffracted X-rays as a function of the angle at which they occur depends upon the manner in which the soap molecules are arranged. The impulses on the Geiger tube were transmitted to a strip-chart potentiometer so that the desired data were recorded automatically.

[7] Characterization of some commercial soaps by X-ray diffraction, Gopal S. Hattiangdi, J. Research NBS 42, 331 (1949) RP1972.

Phase nature of the solids and physico-chemical properties of 2.5-percent solutions of various commercial soaps

Type	Major constituents	Phase	Electrical conductance	Surface tension	pH	Opacity	Rate of growth of foam
			mhos/cc $\times 10^{-4}$	*Dynes/cm.*		*Klett scale divisions*	*Time in seconds per 100 divisions rise*
Toilet	Sodium palmitate Sodium oleate	Beta Omega	27.24	32.00	10.04	390	19
Medicated	Sodium palmitate Sodium oleate	Beta Omega	27.39	32.90	10.07	200	23
Glycerin	Indefinite	Not identified	31.06	34.35	10.00	190	19
Coco	Sodium laurate Sodium myristate	Omega do	27.30	28.45	9.17	2	19
Laundry (washing)	Indefinite	Not identified	43.48	33.04	10.16	46	20
Shaving	Sodium palmitate	2 or more	28.12	34.20	10.04	660	30

A crystalline soap phase, well developed in three dimensions (a, b, and c axes), exhibits a sharp, rather intense long spacing and several short spacings, which are well defined and lead to sharp peaks in the X-ray diffraction pattern. The sharpness of the long and short spacings observed for the various commercial soap patterns therefore indicates that they are all crystalline. X-ray diffraction data have also been used to identify the various phases present in the commercial soaps on the basis of published values of both the long and short spacings for numerous phases of pure sodium laurate, myristate, palmitate, stearate, and oleate. The approximate degree of hydration, based on water (moisture) content, has been computed for the various soaps.

The X-ray diffraction data can be further used to depict the nature of molecular packing in soap crystals. This may be stated briefly as being an end-to-end packing of the soap molecules, the perpendicular distance between two consecutive layers of the polar heads (containing the cation) being the observed value of the long spacing. The distance between hydrocarbon chains of the soap molecules is evidenced as the strong short spacing peak around 4.1 Å. Shorter distances, such as those between carbon atoms in a given soap molecule, may be computed from the values of the relatively weak short spacings exhibited in the region of 2.5 Å. The packing usually takes place with the soap molecules slightly tilted and the angle of tilt, β, can be determined because the true length of the molecules can be calculated from known values of bond angles, bond distances, and atomic radii. The value of β varies from soap to soap and also from one phase state to another.

Phases identified by X-ray diffraction patterns

Type of commercial soap	Phases	Degree of hydration
		Moles of water
Toilet	Mostly beta sodium palmitate; some omega sodium oleate.	0.5 to 1.
Medicated	do	0.5 to 1.
Glycerin	Indefinite	Indefinite.
Coco	Omega sodium laurate and sodium myristate.	2.
Laundry (washing)	Omega phase; soap indefinite.	Indefinite.
Shaving	2 or more phases of sodium palmitate.	1.

Analyses by X-ray diffraction do not always distinguish the components of a binary system because first, a single value of the long spacing may be interpreted as being caused either by a single constituent or by an average of values for two or more distinct forms (two or more separate phases of the same soap or of different soaps); and, second, the short spacing values for two individual soaps or soap phases are unique, but when they are present together the peaks may overlap and their resolution becomes difficult and sometimes questionable. On the other hand, observations by electron microscopy are in excellent agreement with chemical analyses, and in such cases prove to be more rapid and accurate than X-ray diffraction techniques.

As a third phase of this investigation, the physico-chemical properties of solutions of commercial soaps and detergent materials were examined in cooperation with W. W. Walton and J. I. Hoffman for the purpose of interrelating the colloid-chemical nature of the solutions to the phase nature of the solids.[8] Hence, data were obtained on the electrical conductivity, surface tension, pH, opacity, and rate of growth of foam, of aqueous solutions of numerous soaps and detergent materials. Some qualitative observations were also made on the physical behavior of the soaps. Thus, the hardness of the soaps, as observed arbitrarily, decreases in the order toilet-medicated-laundry-shaving, whereas the percentage of soap rubbed off the cake (bar) in use in water is, qualitatively, shaving-toilet-laundry. On standing in water, the toilet and shaving soaps swell and disintegrate, whereas the laundry soaps crack somewhat with little or no swelling.

In most cases, there is no great difference in the value of any of the physico-chemical properties for products in any given type of soap as for example, toilet, coco, or glycerin. X-ray diffraction data and observations by electron microscopy indicate further that the molecular arrangements and surface features (phase nature) of these products are very similar. A correlation between the two thus seems reasonable but has not been attempted quantitatively in the present investigation, mainly for lack of specific details regarding the composition of the products and the various mechanical, thermal, and other treatments received during the manufacturing process.

[8] Some physical chemical properties of aqueous solutions of soaps and soapless detergents, Gopal S. Hattiangdi, William W. Walton, and James I. Hoffman, J. Research NBS **42**, 361 (1949) RP1974.

On plotting the values for each property against the soap content in various solutions, discontinuities are obtained in otherwise smooth and regular curves. The discontinuities occur in two general regions, at approximately 0.1- to 0.2-percent and 2- to 2.5-percent of soap. That in the lower concentration is brought about by the formation of a single layer of the soap molecules on the surface, whereas that in the higher region indicates the formation of soap micelles (ionic micelles) with single or multiple charges. The almost steady values of conductivity and surface tension obtained beyond this higher concentration indicate that both the surface and the interior of the system are saturated with respect to the charged micelles.

The synthetic detergents, on the other hand, are characterized by their ready solubility in cold water. Solutions of these materials may be either acidic or alkaline and have an almost constant value of conductivity and surface tension at high concentrations, and extremely low and constant values of opacity at lower concentrations.

On the basis of colloid-chemical concepts, an efficient cleansing compound should have a low surface tension, a relatively high electrical charge, and ability to form colloidal micelles at low concentration, a property that facilitates solubilization. When the physico-chemical data for solutions of soaps and synthetic detergent materials are considered together, it is seen that greater surface activity and an optimum degree of micelle formation, both in number and in size, are obtained with dilute solutions of synthetic detergents and concentrated solutions of the soaps. Consequently, cleansing should be achieved better and more economically by using soap solutions of relatively high concentrations and synthetic detergent solutions in the lower concentration region.

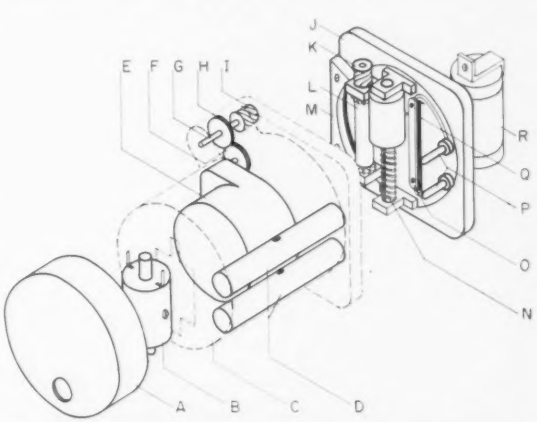
Panel-Type Accelerometer for Aircraft

A novel type of accelerometer,[9] which gives both an instantaneous indication and a record of the acceleration of an airplane in flight has been developed by A. S. Iberall of the National Bureau of Standards for the U. S. Air Force. Outstanding features of the device are compactness, which permits mounting on an instrument panel, and the use of spark recording to obtain a readily available record on a paper chart. The details of the design are such that small panel-type recorders of other physical quantities—temperature, pressure, or voltage, for example—can be similarly constructed to occupy a space not much larger than an ordinary indicating instrument.

The immediate application of the new accelerometer is in the training of aviators for combat flying, where sharp turns must be made at high speeds. Practice in making such turns can be more effectively obtained if the instrument panel of the plane is provided with an accelerometer that gives an instantaneous visual indication of acceleration while the maneuver is being executed. At the same time, it is desirable to have a record of acceleration for quick reference after a flight has been completed. However, the accelerometers that have been available are either too large for instrument-panel mounting or, if small enough for panel use, do not provide an automatic record of acceleration. Moreover, as most recording accelerometers require photographic equipment, interpretation of the trace must usually wait until the film has been developed. The Air Force therefore requested the National Bureau of Standards to initiate the development of a small, compact indicating and recording accelerometer that would meet the requirements of flight-training use.

A sliding bob mounted on a shaft and restrained by a helical spring serves as the acceleration-sensitive element of the device. Acceleration of the aircraft along the axis of the shaft displaces the bob by an amount proportional to the acceleration, at the same time compressing the spring. The varying displacement of the bob from its rest position is permanently recorded on a paper chart by a repetitive high-voltage spark occurring at the position of the bob. An instantaneous indication of acceleration is also obtained, since the record paper is visible through the transparent front of the accelerometer case immediately after puncture.

The accelerometer constructed at the Bureau is built into a rate-of-climb indicator case of the standard aircraft-panel type. By means of the zero-setting shaft of the rate-of-climb indicator, power from a small synchronous timing motor for driving the record chart



A sliding bob mounted on a shaft and restrained by a helical spring serves as the acceleration-sensitive unit (*N*) of a new indicating and recording accelerometer. A high-voltage spark between electrode *O* and a nickel tip on the bob pierces a chart of sensitized paper, thus making a permanent and instantly visible record of the displacement of the bob.

[9] For further technical details, see A novel recording accelerometer, by A. S. Iberall, Rev. Sci. Inst. 20, 304 (1949).

is transmitted from the back to the front of the case without obstructing the available space. Sprocketed rollers mounted just behind the front of the case are thus made to pull the recording paper across the inner face of the cover and push it out the side of the case, where it may be torn off. As the recording paper passes across the face of the instrument, it is punctured by sparks at a 60-cycle repetition rate. The writing electrodes consist of a nickel tip projecting perpendicularly from the bob, and the edge of a narrow strip mounted on the inside of the cover directly under the tip. The bob and nickel tip are made the high-voltage electrode, whereas the plate and other parts are grounded to permit removal of the cover without risk of electrical shock. The high voltage is provided by a small model-airplane spark coil mounted behind the motor. Current is brought to the bob through insulated banana plugs so that removal of the cover for loading the record will cut off the voltage to the electrodes.

The linear speed of the record chart is about 6 inches per minute. The cartridge for storage of the record chart is mounted in a semicylindrical depression in the outside of the transparent plastic cover, which is slotted to receive the tangent lip of the cartridge.

A 35-millimeter single-weight perforated photographic paper with no emulsion was chosen for the record chart. As the thickness of the paper (0.005 inch) required more energy to form an easily visible trace than was available from the small spark coil, a simple preliminary chemical treatment was developed for the paper to intensify the trace as it is formed.

The necessity of operating the accelerometer aboard a plane from a 28-volt source of direct current also required the development of a special power supply. A 60-cycle vibrator is employed in the usual way to produce 60-cycle alternating current for the motor. However, the power dissipation of the small spark coil makes operation by a repetitive voltage "pip" most desirable. This pip is supplied by the inductive decay of the vibrator coil on the "break" of its main reed contact.

In laboratory performance tests at the National Bureau of Standards, the accelerometer successfully withstood shock and vibration of at least 15 *g* units of acceleration. Paper speed was found uniform to within a few percent. The record obtained was easily interpreted and adequate for resolving detail of amplitude not less than 2 percent of the total record width.

Measurement of Intense Low-Voltage X-rays

An important phase of the present X-ray research program at the National Bureau of Standards is concerned with improved techniques for measuring intense low-voltage X-rays. The measurement of X-rays generated by voltages below 50 kilovolts in terms of the international roentgen has always been a problem, but in recent years the situation has become acute. This has been brought about by two tube developments: A contact therapy tube in which the target where the X-rays are produced is placed against the skin or even inserted into the body cavities, and a beryllium-window tube yielding 10,000 times the output of an ordinary X-ray tube. In the first of these, the radiation in the tissues is very intense near the target and it is therefore essential to measure accurately and control the dosage. The second type is used primarily for skin therapy, biological research, and for some industrial purposes where high output is useful.

These low-voltage tubes have found important applications, but users have been forced to measure the radiation with instruments designed for higher voltage ranges. They have generally employed thimble ionization chambers made for ordinary therapeutic X-rays and calibrated over the range of 70 to 200 kilovolts, since it is only within this range that radiation standards have been available. When used in the range of 10 to 50 kilovolts, these chambers may be considerably in error—often as much as 30 percent.

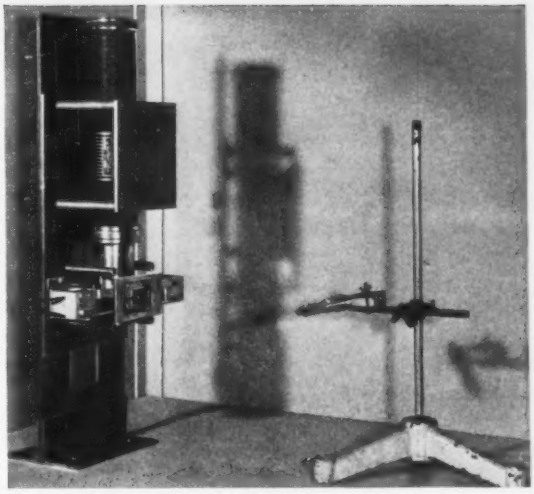
A standard for measuring low-voltage radiations was first produced at the National Bureau of Standards in 1930 and, so far as is known, is the only instrument of this type ever built. It has frequently been loaned to other laboratories for special calibrations. Within the past 2 years, because of the increased interest in the measurement of very soft radiations (10 to 50 kilovolts), the Bureau has intensified work on this problem. The new studies have had two principal directions: First, designing and constructing improved performance standards and, second, obtaining data to permit the approximate correction of standard dosage meter readings for very soft X-rays.

The problem of devising a small free-air standard ionization chamber proved not too difficult for radiation intensities up to 1,000 roentgens per minute, following lines previously established at this Bureau. However, in the use of such a chamber, absorption of the very soft radiation between the diaphragming and measuring point may be very large, and this loss must be known with an accuracy equal to that desired in the final measurement. A large series of such air absorption coefficients has been determined by using a beryllium-window X-ray tube with voltages ranging from 10 to 200 kilovolts in small increments. Since the coefficient of air absorption varies rapidly with the wavelength distribution in the X-ray beam, the results are critically dependent upon the waveform of the voltage used to produce the X-rays. At the Bureau a constant-potential excitation has been used in order to obtain a describable radiation quality.

For radiation intensities above 1,000 roentgens per minute it was discovered that the simple standard could not be used in the normal way. The principal problem was to measure all of the ions produced in the chamber. Because of the very high concentration of ions along the beam, a substantial fraction of the ions is lost by recombination. At the highest usable electric fields in

the chamber (4,000 volts per cm) the losses range from 1 percent at 10,000 roentgens per minute to 10 percent at 300,000 roentgens per minute with a normal beam of about 8-millimeter diameter. It is possible to overcome this difficulty by reducing the beam diameter to 0.5 millimeter so that 100 percent of the ions can be pulled away and measured at field strengths of only 500 volts per centimeter. A successful standard embodying this modification has now been constructed for calibration in the range of 5 to 50 kilovolts. Accurate calibrations have now been made with this standard, for all the commercially available dosage meters, even though the standard was not originally intended for use at such low energies. When properly calibrated, these ionization chambers can be used safely with soft radiations if the intensities are not too great and if the voltage waveform during calibration and subsequent use is the same.

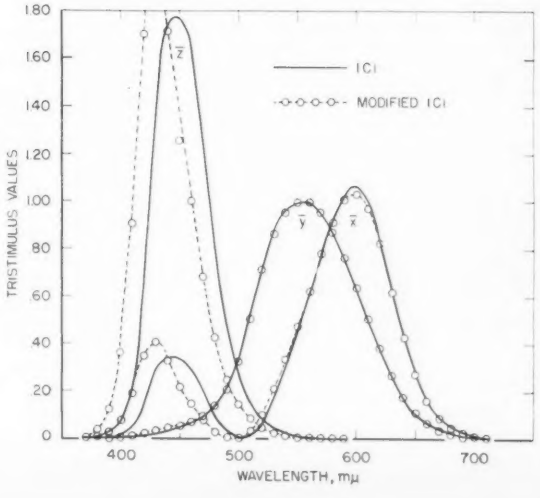
Inherent limitations of the thimble chambers have been discovered for the measurement of high-intensity X-rays (above 1,000 roentgens per minute) in air. Most such chambers operate with an electrode potential ranging from 200 to 400 volts. This voltage is insufficient to pull all of the ions to the collecting electrode before some are lost by recombination. At an intensity of say 5,000 roentgens per minute, the loss may be 5 percent; whereas at 500,000 roentgens per minute it may be as much as 70 percent. Since with present instruments there is no way of substantially increasing electrode potential, the Bureau has experimentally determined saturation curves for high-radiation intensities, from which it is possible to obtain fair corrections for the loss of ions. Since this correction cannot be relied on in all situations met in practice, careful determinations have been made of the limitations and intensity range of such chambers. Although a thimble chamber has not been perfected for every use, it has been established clearly for the first time just when these chambers can be used safely.



An experimental arrangement has been used in the Bureau's X-ray Laboratory to expose a nylon thimble chamber to X-rays from a beryllium-window tube. The tube is mounted behind a solenoid shutter control which admits definite amounts of radiation to the chamber.

Out of these studies have come design principles leading to the possibility of a new type of small ionization chamber suitable for measuring the extremely high intensities yielded by the low-voltage beryllium-window tubes.

ICI Standard Observer for Colorimetry



Recent work at the National Bureau of Standards indicates that the "ICI standard observer", that is, the fundamental data on color mixture that has, since 1931, been accepted internationally for interpreting colorimetric measurements, may need to be revised.[10] This work corroborates findings from three other laboratories in this country; Harvard Medical School, Eastman Kodak Co., and National Lead Co.

Modern colorimetry depends upon a break-down into its component spectral parts of the light entering the eye of the observer. The spectral transmittance of

[10] For further technical details, see "A comparison of direct colorimetry of titanium pigments with their indirect colorimetry based on spectrophotometry and a standard observer," by Deane B. Judd. (NBS, publication pending).

Tristimulus values of the spectrum according to the ICI standard observer are compared with the modified observer devised at the National Bureau of Standards by means of curves which give for each part of the spectrum the amounts of the red (X), green (Y), and blue (Z) primaries required to duplicate the color. The shift of emphasis in the modified functions toward the short-wave extreme of the spectrum is clearly shown.

standard filters and the spectral reflectance of opaque color standards are measured by means of the spectrophotometer. Since its recommendation in 1931 by the International Commission on Illumination, the standard way of interpreting such spectrophotometric information has been by way of the body of fundamental data on color mixture known as the 1931 ICI standard observer. These data have achieved world-wide acceptance for this purpose, and, in the United States, particularly, the ICI standard observer has found its way into hundreds of practical applications.

Considerable interest was therefore aroused by a report from the Titanium Division of the National Lead Co. that the ICI standard observer was not adaptable to the colorimetry of titanium-pigment paints.[11] A. E. Jacobsen found that, when the well-known near-white anatase and rutile titanium dioxide pigments were incorporated in a paint vehicle, they yielded colors that could be distinguished by eye. However, spectrophotometric data reduced by means of the ICI standard observer indicated that the colors were the same. He suggested that the ICI standard observer weights too lightly the spectral region below 430 millimicrons.

[11] A. E. Jacobsen, Nonadaptibility of the ICI system to some near-whites which show absorption in the far-blue region of the spectrum, J. Opt. Soc. Am. **38**, 442 (1948).

As the first step in a study of the phenomenon by Dr. Deane B. Judd of the Bureau's photometry and colorimetry laboratory, a pair of these titanium-pigment paints was examined by seven observers. Four of the seven corroborated Jacobsen's conclusion; three agreed closely with the standard observer. A modification of the standard observer was then derived, based upon the spectral luminosity determinations of Gibson and Tyndall at the National Bureau of Standards and of Wald at the Harvard Medical School. The modified observer was shown to account largely for observations of the group of four observers that disagreed with the standard observer. Since this work, the Gibson-Tyndall-Wald data on spectral luminosity have had striking corroboration by Weaver of Eastman Kodak; his results likewise indicate the standard luminosity function to be too low in the short-wave extreme of the spectrum.

It is recommended that further studies of the luminosity function in this region be conducted, particularly by foreign laboratories, so that a broad and sound basis for a possible revision of the ICI standard observer may be laid. Until such time as a revision is made officially by an international body, however, the Bureau will continue to base its color standards on the 1931 ICI standard observer.

NBS Publications

Periodicals [12]

Journal of Research of the National Bureau of Standards, volume **42**, number 6, June 1949. (RP1991 to RP1999, incl.)

Technical News Bulletin, volume **33**, number 6, June 1949. 10 cents.

CRPL–D58. Basic Radio Propagation Predictions for September 1949. Three months in advance. Issued June 1949. 10 cents.

Nonperiodical

Research Papers [12] [13]

RP1982. The acidic dissociation constant of ammonium ion at 0° to 50° C, and the base strength of ammonia. Roger G. Bates and Gladys D. Pinching. 10 cents.

RP1983. Concrete as a protective barrier for gamma rays from radium. Harold O. Wyckoff and Robert J. Kennedy. 10 cents.

RP1984. Transient vibration in an airplane wing obtained by several methods. Walter Ramberg. 10 cents.

RP1985. The use of plastic replicas in evaluating surface texture of enamels. Joseph C. Richmond and Allen C. Francisco. 10 cents.

RP1986. An electric gage for measuring the inside diameter of tubes. Abner Brenner and Eugenia Kellogg. 10 cents.

RP1987. Effect of boron on the structure and some physical properties of plain cast irons. Alexander I. Krynitsky and Harry Stern. 10 cents.

RP1988. Improved single-unit Schiefer abrasion testing machine. Herbert F. Schiefer, Lawrence E. Crean, and John F. Krasny. 15 cents.

RP1989. Pyrolysis of polyisobutene (Vistanex), polyisoprene, polybutadiene, GR-S, and polyethylene in a high vacuum. Samuel L. Madorsky, Sidney Straus, Dorothy Thompson, and Laura Williamson. 10 cents.

RP1990. Basis of the application of network equations to waveguide problems. David M. Kerns. 15 cents.

Applied Mathematics Series [12]

AMS5. Tables of sines and cosines to fifteen decimal places at hundredths of a degree. 40 cents.

Commercial Standards [12]

CS120–48. Standard stock ponderosa pine doors. (Third edition. Supersedes CS120–46.) 15 cents.

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Simplified Practice Recommendations [12]

R193–49. Packages for shortening, salad oil, and cooking oil. (Supersedes R193–42.) 5 cents.

R207–49. Pipes, ducts, and fittings for warm-air heating and air conditioning. (Supersedes R207–45.) 10 cents.

Articles by Bureau Staff Members in Outside Publications [14]

Stabilization of austenitic stainless steel. S. J. Rosenberg and J. H. Darr. Trans. Am. Soc. Metals (7301 Euclid Ave., Cleveland, Ohio) **41**, 1261 (1949).

Standard fire tests of building materials. H. D. Foster. Engineering Experiment Station News (Ohio State University, Columbus, Ohio.) **20**, No. 4, 9 (Oct. 1948).

Economic aspects of standardization. F. E. Powell. Standards World (P. O. Box 7593, Benj. Franklin Station, Washington 4, D. C.) **1**, No. 2, 59 (1949).

A novel recording accelerometer. A. S. Iberall. Rev. Sci. Instr. (57 East Fifty-fifth Street, New York 22, N. Y.) **20**, 304 (1949).

[12] Send orders for publications under this heading only to the Superintendent of Documents, Government Printing Office, Washington 25, D. C. Annual subscription rates: Journal of Research, $4.50 (foreign $5.50); Technical News Bulletin, $1.00 (foreign $1.35); Basic Radio Propagation Predictions, $1.00 (foreign $1.25). Single copy prices of publications are indicated in the lists.

[13] Reprints from May Journal of Research.

[14] These publications are not available from the Government. Requests should be sent direct to the publishers.

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